

PATENT SPECIFICATION

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NO DRAWINGS

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(54) DYEING AND PRINTING PROCESS FOR TEXTILES AND TEXTILE FIBRES

(71) We, SANDOZ LTD., of 4002 Basle, Switzerland, Lichtstrasse 35, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for dyeing or printing polyester fibres in the form of loose fibre, yarn or piece goods using a disperse dye in the presence of a carrier which contains at least 30% by weight of an alkylbenzene. It is to be understood that the term "polyester fibres" as used throughout this specification includes all fibres having a large number of ester groups in the molecule e.g., fibres of the polyethylene terephthalate type as well as cellulose triacetate and linear polyurethanes. It is known that polyester fibres cannot be satisfactorily dyed by exhaust dyeing methods unless a carrier is present in the dyebath, or unless dyeing is carried out at temperatures above 120° C. under pressure. A great number of carriers have been suggested for this purpose, the best known of which include orthophenylphenol and chlorinated benzenes emulsified in water. The use of the known carriers frequently involves disadvantages such as irritation from the vapour, the toxicity of the vapours and the danger of spotting on the dyed goods. It has now been found that polyester fibres and textiles can be dyed or printed with excellent results by using as a carrier a mixture of aromatic compounds which contains at least 30% by weight of one or more alkylbenzenes, in which the benzene nucleus is substituted by two or more methyl radicals or at least one ethyl, propyl or butyl radical. The use of such a carrier mixture, which, under normal conditions of application, boils at a temperature of from 160° C. to 280° C. inclusively can produce dyeings and prints showing superior levelness (with, for example, no spotting) than those produced in the presence of known carriers for polyester fibres. These carriers can be included in a dyebath with a disperse dyestuff in aqueous dispersion. The new carriers can be obtained, for example, from the residues remaining after distillation in the bulk manufacture of ortho-, meta- or para-xylene or other alkylbenzenes.

The dye carriers thus obtained generally contain more than 50% by weight of one or more alkylbenzenes, in which the benzene nucleus is substituted by two or more methyl radicals or at least one ethyl, propyl or butyl radical. In addition, the residues left after distillation in the manufacture of the above mentioned products usually contain diphenyl and small amounts of one or more of the substances, naphthalene, anthracene, phenanthrene and fluorene. The last-named compounds can, if desired, be eliminated from the distillation residues, in which case dye carriers are obtained which boil in the region of 160° C. to 185° C.

It can be of advantage to employ mixtures of dye carriers which besides the above mentioned aromatic hydrocarbons contain other aromatic compounds, for example diphenyl ether, benzoic acid methylester, or aromatic compounds containing halogen each of which may bear one or more non-water-solubilizing substituents. Examples of non-water-solubilizing substituents are halogen atoms, nitro, cyano, hydroxyl, alkyl and alkoxy groups.

Carrier mixtures used in processes within the present invention have a more balanced effect on dyeing than their single components alone. At room temperature

[Price 25p]

Price 75p

the mixtures can dissolve solid dye carriers such as naphthalene and diphenyl, which if present in the bath alone tend to crystallize and may then interfere with the progress of dyeing.

Conventional dyeing (which includes pad dyeing) and printing methods for polyester fibres can be employed with the carriers conforming to this invention. It is, however, advisable to add the carrier to the dyebath, padding liquor or printing paste in the form of a fine dispersion, or preferably as an aqueous emulsion, in amounts of 2% to 35% in relation to the weight of the material to be dyed or printed. The emulsions are best prepared with emulsifiers, suitable examples being the adducts of ethylene oxide on alkylphenols such as nonylphenol and dodecylphenol or on castor oil, and alkylbenzene sulphonates, dodecylphenoldiphenylether disulphonate, neutralized sulphonates of the condensation products of phenol or naphthalene with formaldehyde, and mixtures of these emulsifiers.

The emulsifier or emulsifier mixture is preferably added to the dye carrier mixture or to a blend of such a carrier mixture and one or more known carriers or solvents, in an amount which generally ranges from 5% to 30% by weight, or preferably 15—25% by weight, based on the amount of the carrier mixture. The emulsifier or emulsifier mixture is preferably prepared with an ionic dispersing agent, preferably in an amount greater than 60% by weight, more especially from 80% to 95% by weight of the emulsific mixture and a non-ionic dispersing agent in amounts of 5% to 15% by weight of the emulsifier mixture. The most suitable anion-active dispersing agents for use with the emulsifiers are those which cause little foaming with the active substance of the carrier mixtures used in processes within this invention in the dyeing process. These anion-active dispersing agents include sulphonated castor oils, sulphonated oleic acid esters, alkyl-naphthalene sulphonates, succinic acid diethyl-hexylester sulphonates, xylene sulphonates and toluene sulphonates. Examples of suitable non-ionic dispersing agents are fatty acid ethers, arylphenol and alkylphenol-polyglycol ethers; if dispersing agents having more than 25—30 ethylene oxide residues per molecule are used these should not form more than 5% by weight of the emulsifier mixture.

Polyglycoether derivatives having approximately 6—15 moles of added ethylene oxide groups per molecule are also moderately useful, especially if they are partially carboxymethylated. Carboxymethylated polyglycoether derivatives having more than 25 ethylene oxide residues per molecule are comparably in their action to non-carboxymethylated emulsifiers of similar ethylene oxide content.

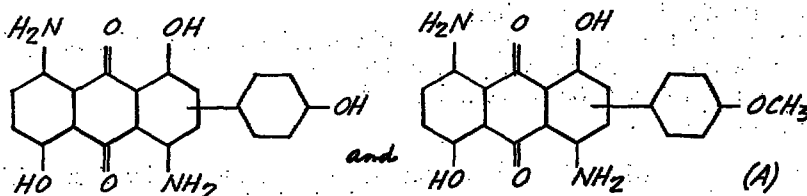
The use of an emulsifier with the highest possible anionic activity is necessary with the active carrier substances used in processes within this invention in order to obtain deep dyeings. If the emulsifier mixture contains too high a percentage of non-ionic emulsifier, it is very difficult to reach deep black dyeings. Conversely, if the emulsifier is only anion-active (e.g. if the specific sulphonates are dodecylbenzene sulphonates), the dye tends to exhaust too rapidly onto the fibre and the dyeings show inferior rubbing fastness. The emulsifier preparations may either be added directly to the dyebath, padding liquor or printing paste, or they may be mixed with a suitable dye and the mixture worked up as a dye preparation. While the process of the present invention is intended *primarily* for the dyeing of textiles made of polyester fibres of high melting point, it is also suitable for use with other hydrophobic fibres of poor dyeability having a large number of ester groups in the molecule, for example cellulose triacetate and linear polyurethanes.

The assistants described herein are highly suitable for use in dyeing and printing with disperse, developed and vat dyes, being applicable in the dyeing or printing process itself or as a separate pretreatment. Conventional dyeing and printing methods for disperse dyes can be employed, the dyes being invariably added to the dyebath in finely dispersed form. The dyed or printed goods can be submitted to a reduction clearing treatment if necessary.

In the following Examples the parts and percentages are by weight and the temperatures are given in degrees centigrade.

Example 1

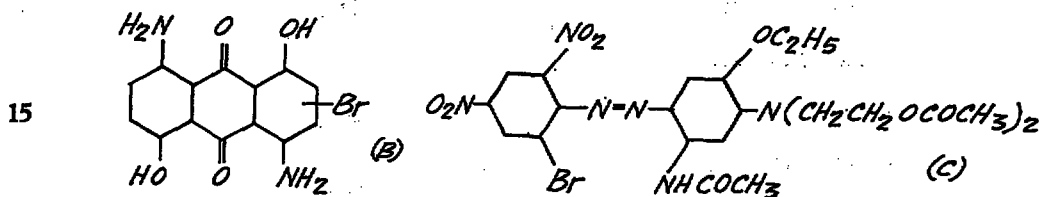
A dye bath is set at 40° with 4000 parts of water, 2 g/l of anhydrous ammonium sulphate, 0.6 parts of a finely dispersed mixture of 50% of each of the dyes of formula



5 and 6 parts of Assistant b.① (see Table), which emulsifies in the bath. The pH is adjusted to 5 with formic acid and 100 parts of a fabric of polyester fibre are entered. In 30 minutes the temperature is raised to about 97° and the fabric dyed for about 1 hour at this temperature. On removal it is washed off, rinsed and dried. A level, well penetrated blue dyeing is obtained on the polyester fabric which has excellent fastness properties.

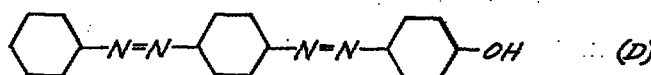
Dyeings of the same good quality are obtained when one of the assistants b.② to ⑤ in the following table is used.

With the disclosed assistants, dyeings of excellent levelness and high fastness can be produced with the dyes of the following formulae

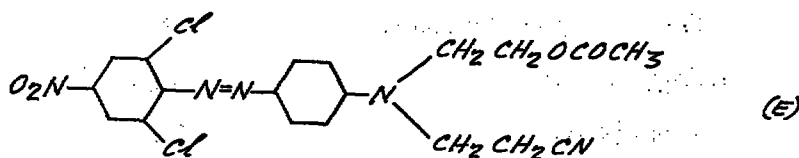


blue

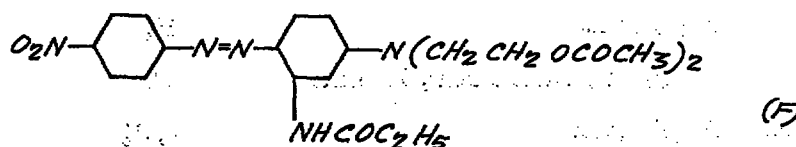
blue



yellow



yellow-brown



scarlet

Example 2

A polyester fabric is printed with a paste of the following composition:

- 30 parts of dye (E) in finely dispersed form,
 630 parts of crystal gum,
 30 parts of di-isobutyl phosphate,
 20 parts of the sodium salt of the disulphonimide of a mixture of hydrocarbons having on the average 12 carbon atoms,
 70 parts of assistant b(2) (in the Table) and
 220 parts of water.

The print is dried at 60—100°, steamed for 20 minutes, rinsed and dried. A yellow-brown print with excellent fastness properties is obtained.

TABLE

a. Dye carrier mixtures

①	1,2,3-Trimethylbenzene,	}	25%
	1,2,4-Trimethylbenzene,		
	1,3,5-Trimethylbenzene		
	1,2-Ethyltoluene	}	45%
	1,3-Ethyltoluene		
	1,4-Ethyltoluene		
	n-Butylbenzene		10%
	sec.-Butylbenzene	}	20%
	tert.-Butylbenzene		
②	1,2,3-Trimethylbenzene		5%
	1,3,5-Trimethylbenzene	}	10%
	tert.-Butylbenzene		
	1,2,4-Trimethylbenzene	}	16%
	sec.-Butylbenzene		
	ortho-, meta, para-Ethyltoluene		27%
	n-Propylbenzene		8%
	Isopropylbenzene		3%
	n-Butylbenzene		5%
	Diphenyl		20%
	Naphthalene		1%
	Anthracene, Phenanthrene, Fluorene		5%
③	Ethylbenzene		0.5%
	para-Xylene		1%

TABLE (continued)

meta-Xylene	2%
ortho-Xylene	3%
Isopropylbenzene	1%
meta-Ethyltoluene	} 20%
para-Ethyltoluene	
1,3,5-Trimethylbenzene	7%
ortho-Ethyltoluene	} 6,5%
Isobutylbenzene	
1,2,4-Trimethylbenzene	30%
n-Propylbenzene	4,5%
sec.-Butylbenzene	0,5%
1,3-Diethylbenzene	1,5%
1,4-Diethylbenzene	} 8,5%
n-Butylbenzene	
1,2,3-Trimethylbenzene	
4-tert.-Butyltoluene	1%
1,2-Diethylbenzene	2%
Indole	2%
Content of undetermined higher aromatics solvents	9%
④ 30% of mixture 1, 40% Diphenylether, 12,5% Diphenyl and 17,5% Naphthalene	
⑤ 30,0% of mixture 1, 5% Chloronaphthalene, 5% Benzoic acid methyl ester, 10% Tetralin, 12,5% Diphenyl, 17,5% Naphthalene and 20% Diphenylether.	

TABLE (continued)

b. Assistants (mixtures of dye carriers and emulsifiers)

- ① 80% Dye carrier mixture a. ①,
10% Castor oil polyglycolether (30 moles ethylene oxide)
and 10% Sodium dodecylbenzenesulphonate.
- ② 75% Dye carrier mixture a. ②,
13% Castor oil polyglycolether (30 moles ethylene oxide)
and 12% Sodium dodecylbenzenesulphonate.
- ③ 80% Dye carrier mixture a. ③,
10% Castor oil polyglycolether (30 moles ethylene oxide)
and 10% Sodium dodecylbenzenesulphonate.
- ④ 80% Dye carrier mixture a. ④,
10% Nonylphenol polyglycolether (10 moles ethylene oxide),
5% Castor oil polyglycolether (30 moles ethylene oxide)
and 5% Monoethanolamine salt of n-dodecylbenzenesulphonic acid.
- ⑤ 75% Dye carrier mixture a. ⑤,
13% Nonylphenolpolyglycolether (10 moles ethylene oxide),
6% Castor oil polyglycolether (30 moles ethylene oxide)
and 6% Monoethanolamine salt of n-dodecylbenzenesulphonic acid.

WHAT WE CLAIM IS:—

1. A dyeing or printing process in which polyester fibres in the form of loose fibre, yarn or piece goods are dyed or printed with a disperse dye in the presence of a dye carrier, which is a mixture of aromatic compounds containing at least 30% by weight of one or more alkylbenzenes in which the benzene nucleus is substituted by two or more methyl radicals or at least one ethyl, propyl or butyl radical which dye carrier boils at a temperature of from 160° C. to 280° C. inclusively.
2. A process according to Claim 1, wherein the dye carrier contains diphenyl and small amounts of one or more of the substances naphthalene, anthracene, phenanthrene and fluorene.
3. A process according to Claim 1, wherein the dye carrier further contains a diphenylether which is optionally substituted by one or more non-water-solubilizing groups.
4. A process according to any one of the preceding claims, wherein the polyester fibres are dyed or printed in the additional presence of 5% to 30% by weight based on the weight of the carrier of an emulsifier which contains more than 60% by weight of an anion-active dispersing agent, and 5 to 15% by weight of a non-ionic dispersing agent.
5. A dye liquor for dyeing or printing polyester fibres in the form of loose fibre, yarn, or piece goods, which liquor contains a disperse dyestuff in aqueous dispersion and a dye carrier which contains at least 30% by weight of an alkylbenzene in which the benzene nucleus is substituted by two or more methyl radicals or at least one ethyl, propyl or butyl radical, which dye carrier boils at a temperature of from 160° C. to 280° C. inclusively.
6. A process for dyeing or printing polyester fibres according to any one of claims 1 to 4 substantially as herein described and exemplified.
7. Polyester fibres whenever dyed or printed by a process according to any one of claims 1 to 6.

TABLE (continued)

b. Assistants (mixtures of dye carriers and emulsifiers)

- ① 80% Dye carrier mixture a. ①,
10% Castor oil polyglycolether (30 moles ethylene oxide)
and 10% Sodium dodecylbenzenesulphonate.
- ② 75% Dye carrier mixture a. ②,
13% Castor oil polyglycolether (30 moles ethylene oxide)
and 12% Sodium dodecylbenzenesulphonate.
- ③ 80% Dye carrier mixture a. ③,
10% Castor oil polyglycolether (30 moles ethylene oxide)
and 10% Sodium dodecylbenzenesulphonate.
- ④ 80% Dye carrier mixture a. ④,
10% Nonylphenol polyglycolether (10 moles ethylene oxide),
5% Castor oil polyglycolether (30 moles ethylene oxide)
and 5% Monoethanolamine salt of n-dodecylbenzenesulphonic acid.
- ⑤ 75% Dye carrier mixture a. ⑤,
13% Nonylphenolpolyglycolether (10 moles ethylene oxide),
6% Castor oil polyglycolether (30 moles ethylene oxide)
and 6% Monoethanolamine salt of n-dodecylbenzenesulphonic acid.

WHAT WE CLAIM IS:—

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2. A process according to Claim 1, wherein the dye carrier contains diphenyl and small amounts of one or more of the substances naphthalene, anthracene, phenanthrene and fluorene. 10
3. A process according to Claim 1, wherein the dye carrier further contains a diphenylether which is optionally substituted by one or more non-water-solubilizing groups. 15
4. A process according to any one of the preceding claims, wherein the polyester fibres are dyed or printed in the additional presence of 5% to 30% by weight based on the weight of the carrier of an emulsifier which contains more than 60% by weight of an anion-active dispersing agent, and 5 to 15% by weight of a non-ionic dispersing agent. 20
5. A dye liquor for dyeing or printing polyester fibres in the form of loose fibre, yarn, or piece goods, which liquor contains a disperse dyestuff in aqueous dispersion and a dye carrier which contains at least 30% by weight of an alkylbenzene in which the benzene nucleus is substituted by two or more methyl radicals or at least one ethyl, propyl or butyl radical, which dye carrier boils at a temperature of from 160° C. to 280° C. inclusively. 25
6. A process for dyeing or printing polyester fibres according to any one of claims 1 to 4 substantially as herein described and exemplified.
7. Polyester fibres whenever dyed or printed by a process according to any one of claims 1 to 6.



8. A dye liquor according to claim 5 substantially as herein described and exemplified.

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